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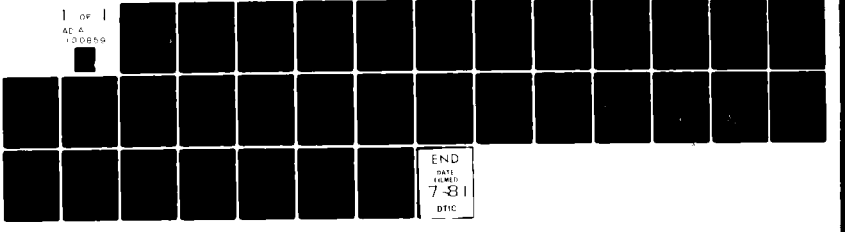

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A new method is introduced for the measurement of photochemical or photobiological reaction rates. Based on linear response theory, the method uses a randomly modulated light source rather than a pulsed one, and employs cross-correlation analysis to extract the desired kinetic information. In operation, a randomly varying light source illuminates the reaction of interest, and the resulting fluctuations in reactant (or product) concentrations are monitored. Mathematical or instrumental cross correlation of the light source variations with those in component concentration then produces the familiar kinetic

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decay curve. Because the new method produces only minute concentration fluctuations, it can measure reaction rates very near equilibrium; moreover, equilibrium position can be shifted by superimposing on the fluctuating light intensity a dc level. Also, because cross correlation is employed, the method enjoys high signal-to-noise ratios. In the present study, the utility and practicability of the new technique are demonstrated through examination of the recombination kinetics of photolytically generated iodine atoms.

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STOCHASTIC PHOTOLYSIS: A NEW METHOD FOR MEASURING RATES OF PHOTOSENSITIVE REACTIONS

by

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INTRODUCTION

The most common means of measuring the rates of photolytic reactions involves the use of a flashlamp and a reaction monitor. In such an approach, the lamp is flashed to initiate the reaction, and the monitor records the reaction progress. Unfortunately, this scheme usually drives the reaction far from equilibrium and requires fast flashlamps and detection equipment. In the present paper, a new method is introduced for measuring fast photolytic reaction rates which overcomes these obstacles. Based on mathematical correlation analysis, the method is capable of determining the rates of reversible reactions which are photolytically driven at varying, selected levels of incident light flux. Although the current implementation of the method employs a laser as a light source, it is equally possible to use conventional lamps; moreover, because the new technique inherently incorporates signal averaging, the lamp need not be particularly intense to yield accurate kinetic data. To demonstrate the viability of the new approach, the well characterized photolysis of gas-phase I_2 was examined.

The basis of the new method lies in the field of linear response theory (Gaskill, 1958; Habil, 1967; Horlick and Hieftje, 1980) and it is from the standpoint of this field that the technique can best be understood. From this standpoint, a conventional flash photolysis experiment is an attempt to measure the impulse response function of a light-sensitive chemical or biological reaction. Ideally, the exciting light pulse will be infinitely short (i.e., resemble an impulse) and the detector used to monitor the reaction will respond with infinite speed, if necessary. Because such a pulse is infinitely narrow, it contains all frequencies at equal amplitude; that is, its Fourier transform is flat (McGillem and Cooper, 1974). Therefore, exciting the probed reaction with the pulse is equivalent to perturbing it simultaneously with all frequencies. Hence, the response of the reaction to the pulse (i.e., the impulse response function) is, in essence, similar to its frequency response, but registered in the time domain. That is, each of the infinite frequency components in the perturbing impulse would also be present in the response of the reaction to the pulse if the reaction were instantaneous. However, because the reaction will proceed at a characteristic rate, the response waveform (as indicated by the detector or reaction monitor) will have

lost some frequency components, while others will have been phase-shifted or distorted. The result will be the familiar photolytic decay curve.

Interestingly, a random waveform (i.e., white noise), like an impulse, also contains all frequencies and at the same amplitude, suggesting that it could be used as an alternative perturbing waveform for photolytic reaction measurements. However, the frequency components in a random waveform have random phases, whereas in an impulse, all components are phase-registered (Beauchamp, 1973). For this reason, the response of a photolytic reaction to a randomly varying light source will not resemble a conventional decay waveform, but will itself appear random. In this apparently random response, however, will be the reaction-rate information; to extract the information, a correlation procedure can be used.

Correlation is simply a mathematical or instrumental procedure which is capable of phase-registering the frequency components within a waveform (autocorrelation) or between two waveforms(cross correlation). As such, cross correlation between a randomly varying perturbing waveform (i.e., the light source fluctuations) and the apparently random fluctuations in reaction equilibrium which it elicits is capable of producing a conventionally appearing impulse response function useful for deducing the rate of a photolytic reaction.

Mathematically, the behavior of a linear system (such as a first-order chemical reaction) can be described by the differential equation

$$a_1 \frac{dx(t)}{dt} + a_0 x(t) = y(t) \qquad (1)$$

where x(t) is the output (response) created by the perturbing input signal y(t). In a conventional flash photolysis experiment, y(t) resembles a mathematical delta function so the response it elicits [x(t)] is by definition the impulse response function. However, if y(t) is a randomly varying perturbation, no analytically usable expression can be written for it, instead the solution can be obtained through use of the convolution theorem. From this theorem, cross-correlation functions, $C_{xy}(\tau)$, fully retain the relative amplitude and phase characteristics of two waveforms, x(t) and y(t), which are

correlated (Gaskill, 1978, Habil, 1967; Horlick and Hieftje, 1980). Thus, we may correlate y(t) with itself to yield the autocorrelation fuction $C_{yy}(\tau)$:

$$\lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{+T} y(t)\left[a_1 \frac{dx(t+\tau)}{dt} + a_0\, x(t+\tau)\right]dt = C_{yy}(\tau) \qquad (2)$$

or

$$a_1 C_{xy}(\tau) + a_0 C_{xy}(\tau) = C_{yy}(\tau) \qquad (3)$$

From the definition of correlation, it is apparent that $C_{xy}(\tau) = \frac{dC_{xy}(\tau)}{d\tau}$. Therefore, Eq. 3 becomes

$$a_1 \frac{dC_{xy}(\tau)}{d\tau} + a_0\, C_{xy}(\tau) = C_{yy}(\tau) \qquad (4)$$

which is identical in form to Eq. 1. However, the perturbing waveform y(t) has been replaced by its autocorrelation function $C_{yy}(\tau)$ and the elicited response by its cross correlation with y(t). Accordingly, if the autocorrelation function of a perturbing signal is a delta function (impulse), the cross correlation of that function with the response it generates will be the impulse response function. Conveniently, white noise produces such an impulse when autocorrelated and this serves as a suitable waveform for photolytic measurements. Hence the term "stochastic photolysis."

An alternative approach to stochastic photolysis would involve measuring directly the frequency response of the photolytic reaction. In this scheme the randomly varying light source would again induce apparently random displacements in the equilibrium position of the reaction being probed. However, the frequency content of these displacements would be measured directly. From the Wiener-Khinchin theorem, this scheme is similar to that employing correlation, since the power spectrum of a waveform is simply the Fourier transform of its autocorrelation function. Similarily the cross-power

spectrum is just the Fourier transform of the cross correlation function. Consequently, Eq. 1 can be represented in the frequency domain as

$$a_1 (j\omega) X(\omega) Y(\omega) + a_0 X(\omega) Y(\omega) = Y(\omega) Y(\omega) \tag{5}$$

where $X(\omega)\ Y(\omega)$ is the cross-power spectrum between the perturbing time function $y(t)$ and its elicited response $x(t)$. In Eq. 5, capital letters denote the frequency (ω) domain representation of the lower-case time function, and j is the imaginary operator. Rearranging Eq. 5 yields

$$X(\omega)\ Y(\omega) = \frac{Y(\omega)\ Y(\omega)}{\sqrt{a_1^2\ \omega^2 + a_0^2}}\ e^{j\tan^{-1}\left(\frac{a_1\omega}{a_0}\right)} \tag{6}$$

Conveniently, if the perturbation $y(t)$ is either an impulse or random waveform, its spectrum is flat; that is, $Y(\omega) = k$, where k is a constant. Therefore, the desired frequency response (cross-power spectrum) of the photoyltic reaction is:

$$X(\omega)\ Y(\omega) = \frac{k^2}{\sqrt{a_1^2\ \omega^2 + a_0^2}}\ e^{j\tan^{-1}\left(\frac{a_1\omega}{a_0}\right)}. \tag{7}$$

The viability of these general approaches have been proven in other areas of application. In some cases, periodic (e.g., sine wave or repetitive pulse) perturbations were employed while in others a random or pseudo-random perturbation (as in the present study) was used. In fact, the methods encompass even those involving the common rotating sector chopper and other modulation schemes for measuring reaction kinetics (Phillips, 1973; Koda, et al., 1977). In such schemes, it is often the phase shift portion of the frequency response which is utilized (cf. Eq. 7). In similar frequency-based studies, pressure modulation of gas/surface systems was used to investigate simultaneous

adsorption at different types of surface sites (Naphtali and Polinsky, 1963; Yasuda, 1976a, b; Yasuda and Saeki, 1978; Clegg and Maxfield, 1976).

Stochastic modulation of the exciting light intensity has been utilized in the determination of fluorescence lifetimes, by either correlation-based (Ramsey, et al., 1979) or frequency response (Hieftje, et al., 1977) measurements. Similarly, the inherent thermodynamic noise which affects a system at equilibrium has been employed to study biochemical and biophysical reactions and diffusion rates (Magde, et al., 1972; Elson and Magde, 1974; Elson and Webb, 1975; Luk'yanchikova, et al., 1976; Chen, 1970; Chen, 1973; Chen, 1978). Such methods, which depend upon autocorrelating spontaneous fluctuations in local component concentrations, are still under development, but show great promise for studying the kinetics of phenomena at equlibrium.

In the present study, a randomly modulated light source and cross correlation techniques are demonstrated to provide kinetic information about photolytic reactions. In particular, the recombination kinetics of photolytically generated iodine atoms are examined. Although this reaction is not first-order and, therefore, not linear, it can be converted to a pseudo-linear system by the creation of a photostationary state. Such an approach broadens considerably the scope of application of stochastic photolysis.

EXPERIMENTAL

Iodine was chosen for the present feasibility study simply for instrumental convenience; its photochemistry matched handily the wavelengths available from an existing laser system and its recombination kinetics occurred on a time scale compatible with the hardware correlator at hand. Specifically, iodine dissociates when irradiated at wavelengths below 499 nm but fluoresces when irradiated at longer wavelengths (Calvert and Pitts, 1966). Therefore, the 488 nm radiation from an argon-ion laser photolyzes the iodine vapor while 514.5 nm light from the same laser can be used to stimulate fluorescence from the remaining molecules. The optical arrangement is shown in Figure 1.

In Figure 1, the laser (Spectra-Physics model 171) is operated in a continuous-wave, all-lines mode at 10 W ouput power. The two desired lines, 488 and 514.5 nm, are dispersed outside the laser cavity by a prism and

separated into two parallel beams by front-surface mirrors. The photolysis beam at 488 nm is modulated in intensity by means of a KDP (potassium dihydrogen phosphate) Pockels cell light modulator (Laserметrics model EOM-703M) placed between two crossed polarizers. The intensity of the 488 nm beam that is transmitted by this apparatus is proportional to the angle through which the KDP crystal rotates its plane of polarization. In turn, this rotation angle is proportional to the voltage applied to the modulator if the modulator is biased into the linear region of the "S"-shaped curve representing the degree of rotation vs voltage.

It is important that the fluorescent probe beam (514.5 nm) interrogate only the region in the sample vessel where photolysis occurs and in a region where the effects of mass diffusion and wall recombination are avoided. Accordingly, the modulated photolysis beam (488 nm) was expanded slightly and recombined with the probe beam at a polarizer. The coaxial beams were then focused through the center of the iodine optical cell (cf. Fig. 2) and reflected back through the cell from a first-surface mirror. Fluorescence of the undissociated iodine molecules is focused onto the entrance slit of a 0.2 m monochromator (J-Y model H20) and passed to a photomultiplier (RCA no. 31034).

Variation in the 488 nm photolysis beam power results in a change in I_2 fluorescence in the expected manner, as seen in the spectra of Fig. 3A. In Fig. 3A, curve 1, the blue (488 nm) beam is off, whereas in Figure 3A, curve 2, the beam intensity is adjusted by means of the KDP modulator to photolyze approximately 10% of the I_2 molecules in its path. Under these conditions, a photostationary state is created, so that small variations in the modulator voltage produce proportional changes in the beam intensity and in the stationary state concentrations. This pseudo-linear behavior is amenable to treatment by the correlation or frequency response methods described earlier.

The iodine vapor cell is protrayed schematically in Fig. 2. Iodine (Baker and Adamson resublimed reagent grade) pressure was controlled by the temperature, T_{I_2}, of a reservoir of solid iodine. The sublimation partial pressure, P, was calculated from the equation (Gillespie and Fraser, 1930)

$$\log_{10} P(\text{atm}) = \frac{-3512.8}{T_{I_2}} - 2.013 \log_{10} T_{I_2} + 13.740 \qquad (8)$$

The temperature of the cell, T_c, was always greater than or equal to that of the reservoir of solid, to minimize deposition of solid I_2 in the cell; similarly, the temperatures of tubing, valves, and side-areas leading to the cell were always greater than that of the cell itself. The cell was 22 mm diameter and 53 mm long and was enclosed in a thermally isolated aluminum block. Heaters in the block were controlled by thermocouples imbedded in it. The I_2 reservoir (a Pyrex finger) was inserted into an aluminum cylinder equipped with a heater; temperature of the reservoir was controlled from a thermocouple affixed to its side. To the vapor-phase I_2 present in the cell was added 100 T of argon, to broaden somewhat the rather narrow features of the I_2 spectrum (cf. Fig. 3B) and thereby obviate a possible spectral mismatch with the exciting laser line.

The experimental electronic arrangement is depicted in Fig. 4. The stochastic perturbation waveform was derived from a binary noise generator (Hewlett-Packard model 3722) adjusted for an infinite sequence length, a clock period of 100 μs and a duty cycle of 50%. This low-voltage waveform was increased to 750 V by the modulator amplifier of Fig. 5; a monitor output from the amplifier (attenuated 1:200) was used as the reference for the perturbing waveform and was sent into one input of the electronic correlator (Hewlett-Packard model 3721A). A dc bias was added to the modulating waveform driving the light modulator by means of a bias insertion unit; this dc bias creates the photostationary state necessary to produce pseudo-linear behavior. The electronic signal from the photomultiplier tube was amplified using the system of Fig. 6 before being directed into the other channel of the correlator. This amplifier was dc coupled to the photomultiplier but ac coupled to the correlator and had a bandwidth of dc to 20 kHz at a gain of 10^7 and a bandwidth of dc to 100 kHz at a gain of 10^6.

RESULTS

A homogeneous mechanism that can be used to interpret the recombination kinetics of photolytically generated iodine atoms is (Porter and Smith, 1961; Bunker and Davidson, 1958; Christie, et al., 1955; Britton, et al., 1956; Marshall and Davidson, 1953; Rabinowitch and Wood, 1936; Strong, et al., 1957):

$$I_2 + h\nu \xrightarrow{\sigma} 2I$$

$$2I + Ar \xrightarrow{k_2} I_2 + Ar, \text{ and}$$

$$2I + I_2 \xrightarrow{k_2} I_2 + I_2.$$

The differential equation expressing the instantaneous concentration of iodine molecules stipulated by these reactions and the experimental conditions is

$$\frac{d[I_2(t)]}{dt} = -\sigma L(t)\,[I_2(t)] + k_2[Ar][I(t)]^2 + k_3[I_2(t)][I(t)]^2 \qquad (9)$$

where σ represents the cross-section for the photolytic generation of iodine atoms and $L(t)$ denotes the number of photons per second irradiating the system. The concentrations (moles/L) of the different species are represented by the symbol for the specific species enclosed in brackets, [ ]. Although Eq. 9 describes a non-linear system, linear behavior can be simulated by establishing a photostationary state which is perturbed on a small scale by concentration noise. The conditions for the photostationary state are

$$L(t) = L(0) + \ell(t) \text{ and} \qquad (10)$$
$$[I_2(t)] = [I_2(0)] + [i_2(t)]$$

where $L(0)$ and $[I_2(0)]$ are the stationary-state values, $\ell(t)$ and $[i_2(t)]$ are the corresponding small-scale departures from these values and where $\ell(t) < L(0)$ and $[i_2(t)] < [I_2(0)]$. Under stationary-state conditions (where $\frac{d[I_2(t)]}{dt} = 0$), Eq. 9 can be used to establish the following relationship between $L(0)$ and $I_2(0)$

$$0 = -\sigma L(0)\,[I_2(0)] + 4k_2[Ar]\{C-[I_2(0)]\}^2 + 4k_3[I_2(0)]\{C-[I_2(0)]\}^2 \qquad (11)$$

where C represents the initial concentration of molecular iodine. Equations 9 and 11 can now be combined to yield an expression which can be simplified by

dropping all second-order terms involving time-dependent phenomena (i.e., i(t) and L(t)). Neglecting these terms is justified by the stated condition that such time-dependent fluctuations would be small compared to the corresponding steady-state values. This operation yields

$$\frac{d\left[i_2(t)\right]}{dt} = -\sigma\ell(t)\left[I_2(0)\right] - 8k_2\left[Ar\right]\left\{C - \left[I_2(0)\right]\right\}\left[i_2(t)\right] - 4k_3\left\{2\left[I_2(0)\right]\left\{C - \left[I_2(0)\right]\right\} - \left\{C - \left[I_2(0)\right]\right\}^2\right\}\left[i_2(t)\right] \qquad (12)$$

Equation 12 can be solved in the frequency domain (via Fourier transformation) to give

$$I_2(\omega) = \frac{-\sigma L(\omega)\left\{C - \frac{1}{2}\left[I(0)\right]\right\} e^{-j\phi}}{\left\{\left\{4k_2\left[Ar\right]\left[I(0)\right] + 4k_3\left[I(0)\right]\left(C - \frac{1}{2}\left[I(0)\right]\right)\right\}^2 + \omega^2\right\}^{\frac{1}{2}}} \qquad (13)$$

and

$$\phi = \tan^{-1}\left[\frac{-\omega}{4k_2\left[Ar\right]\left[I(0)\right] + 4k_3\left[I(0)\right]\left\{C - \frac{1}{2}\left[I(0)\right]\right\}}\right] \qquad (14)$$

where $I_2(\omega)$ and $L(\omega)$ are the frequency-domain equivalents of $i_2(t)$ and $\ell(t)$, respectively, and ϕ is phase. Also, $\left[I(0)\right] = 2\left\{C - \left[I_2(0)\right]\right\}$.

In the present experiment, it is the cross correlation between $\ell(t)$ [the perturbing light waveform] and $i_2(t)$ [the fluorescence of I_2 molecules] which is measured. This cross correlation is the time-domain analog of the cross-power spectrum between $L(\omega)$ and $I_2(\omega)$, which can be otained from Eq. 13 by multiplication:

$$L(\omega)\, I_2(\omega) = \frac{-\sigma L^2(\omega)\, C - \frac{1}{2}\, I(0)\, e^{-j\phi}}{\left\{4k_2\left[Ar\right]\left[I(0)\right] + 4k_3\left[I(0)\right]\left(C - \frac{1}{2}\left[I(0)\right]\right)^2 + \omega^2\right\}^{\frac{1}{2}}} \qquad (15)$$

However, because $\ell(t)$ has the waveform of white noise, its spectrum is flat, so $L(\omega)$ can be replaced by a constant.

Significantly, Eq. 15 represents the frequency response of the I_2 system to photolysis and is, in shape, a Lorentzian, with a maximum at zero frequency whose value can be related to $\frac{[I(0)]}{2L(0)}$, the quantum yield for the photostationary state. This Lorentzian shape betrays the exponential time behavior expected for this pseudo-first-order process. In fact, it can be shown (Hieftje, et al., 1977) that the time constant of such an exponential is equal to the reciprocal of the squared left-hand term in the denominator of Eq. 15. In turn, the half-life, $t_{\frac{1}{2}}$, of the exponential (a more conveniently measurable parameter) is just the time constant times ℓn2.

From these facts, one can derive the following relation from Eq. 15.

$$k_3 = \frac{\ell n2 - 4t_{\frac{1}{2}}\, k_2 [Ar]\, CR}{4t_{\frac{1}{2}} [1 - \frac{1}{2}R] RC^2} \qquad (16)$$

where $R = \frac{[I(0)]}{C}$. The value of R can be calculated from a known value of the initial concentration of iodine vapor (C) and measurements of the cell absorption with the steady-state photolysis beam on and off. Thus, from Eq. 16, measured values of $t_{\frac{1}{2}}$, and tabulated values for k_2 (the recombination rate of iodine atoms using Ar as a third body), values for k_3 can be evaluated.

To evaluate k_3 using Eq. 16 requires that the perturbing noise waveform and the detection system have bandwidths that exceed the frequency response (cf. Eq. 13) of the photolytic reaction. This condition was tested by scattering a portion of the photolysis (488 nm) beam from the front surface of the sample cell and cross-correlating the resulting signal with that from the modulating amplifier monitor (cf. Fig. 5). The resulting cross-correlogram resembled a delta function on the time scale of a typical photolytic experiment, indicating that instrument response was fast enough to obviate the necessity of later deconvolution.

A typical cross-correlation between exictation beam noise (488 nm) and the induced fluctuations in I_2 fluorescence is displayed in Fig. 7. From the excellent fit to an exponential shown in Fig. 7, the photolytic system appears

to follow pseudo-first-order behavior and is therefore amenable to treatment by the procedure described above. From the half-lives of the calculated exponentials fit (using a least squares procedure) to cross-correlograms like Fig. 7, values of k_3 could be calculated.

Experimental parameters and literature values required for the evaluation of k_3 (cf. Eq. 16) are listed in Table I; the resulting k_3 values are also tabulated. Interestingly, the rate constant for iodine atom recombination using I_2 molecules as a third body (k_3) is not sensitive to small variations in k_2, the rate constant for recombination using Ar as a third body. However, the partial pressure of iodine molecules and cell temperature exert a much greater influence on k_3. Unfortunately, these two system variables are not completely independent in the present study, since $[I_2]$ is controlled by heating a reservoir of solid I_2 within the cell. Of the two, cell temperature would be judged to have the greater effect, although the observed change in k_3 with temperature would require an activation energy of -10.9 kcal/mole instead of the value of -5.3 kcal/mole reported in flash-photolysis studies (Porter and Smith, 1961; Bunker and Davidson, 1958). Indeed, a comparison of k_3 determined in the present study with values obtained by other workers (Table II) reveals close agreement with recent studies for measurements near room temperature, but substantial differences at higher temperatures. This pattern can possibly be explained by the sensitivity of the iodine atom recombination rate to wall-induced collisions, an effect which is more pronounced at higher temperatures (Rabinowitch and Wood, 1936). In flash photolysis experiments, such heterogeneous recombination might skew results somewhat; however, in the present experiments, all effects should be negligible. The low-temperature flash photolysis experiments are consistant with an activation energy of -9.0 kcal/mole as shown in Appendix A.

DISCUSSION

Correlation techniques can be utilized to determine the frequency response of chemical systems. The nature of this frequency response can often be used to diagnose the physical, biological, and chemical kinetic parameters of the system. In the time domain, a linear system can be completely characterized

by perturbing it with an impulse (an infinitely narrow pulse) and observing the resulting relaxation processes. Such measurements form the basis of the well-known methods of temperature-jump, pressure-jump, and flash photolysis kinetic observations. The same information can be obtained in real-time noise analysis. A major advantage of the correlation techniques is they can be applied during the system's normal operation. Contrarily, impulse methods can result in overload conditions, thereby modifying the measurement; alternatively, the perturbing impulse must be reduced to such a small amplitude that the resulting output will be partially masked by system noise. As an example the reaction rate of a flow-system could be measured using stochastic perturbation at a single location without varying the flow rate and while the system is operating normally. This approach would be extremely useful, for example, in process control if the rate of reaction were the parameter to be optimized and it were inappropriate to interrupt the flow.

Another advantage of stochastic perturbation is the improved signal-to-noise ratio it provides. Cross correlation is itself a powerful signal enhancement technique. Moreover, the modulation implicit in the stochastic approach shifts the signal information away from zero frequency, reducing 1/f noise. In addition, cross correlation can be performed continuously, allowing the signal information to be updated in real time.

Slow, moderate (DC to hundreds of MHz) or ultra-fast (GHz-THz) kinetics can all be studied by using the appropriate noise source. Slow or moderate reaction rates could be investigated by generating concentration fluctuations by means of a noise-perturbed light source (discharge or arc lamp) or microwave plasma. The unique properties of lasers permits their use over this entire spectrum of kinetics; slow, moderate and ultra-fast. Slow or moderate relation processes can be studied using noise superimposed upon laser radiation by means of either an electrooptical cell or cavity dumper. The study of ultra-fast relaxation processes are amenable to perturbation by laser-mode noise (Hieftje, et al., 1977). Laser mode noise is a nearly ideal perturbation source in that the laser output possesses a DC component which can drive the normal kinetic behavior while the mode-noise probes the relaxation processes.

It should be evident from the discussion in this article that mode-locking a laser is the time-domain equivalent of the mode noise approach. However, using the laser in a mode-locked configuration is never 100% efficient, and involves a reduction in bandwidth of the source.

The use of laser beams in a stochastic perturbation scheme permits unique selection of a subsystem to be probed. For example, relaxation processes in an extremely small volume can be examined. If this volume becomes small enough, the natural concentration fluctuations must be taken into account in the noise analysis (Magde, et al., 1074), since this small sample volume is most likely an open system. Applications using such "fundamental noise" perturbation are likely to have great biochemical importance. The spatial coherence of lasers can be used, as in the present study, to interrogate chemical kinetics in regions isolated from wall effects, and thereby avoid heterogeneous surface reactions, thermal and concentration gradients caused by the proximity of the wall, and stagnant flow at the wall.

The new stochastic perturbation/correlation technique appears in some cases much more specific, sensitive, and convenient than conventional approaches; and the method of perturbation introduces less distortion into the reaction process being measured. The technique is now being applied in our laboratories to the study of metathesis reactions involving a radical. These systems are pseudo-first-order and, consequently, represent linear systems. The kinetic parameters of such systems can be measured by stochastically varying the radical concentration and cross correlating this variation with the induced fluctuations in concentration of reaction partners or products. Chemical kinetic investigations involving thermal-noise, pressure-noise, and hydrogen ion-noise perturbations are also in preparation.

APPENDIX A

Estimation of the Activation Energy for Iodine Atom Recombination from Published Low-Temperature Flash-Photolysis Experiments

Iodine atom recombination involves an elementary atom transfer reaction between the atom and a long-lived complex (Benson, 1968):

$$I + I_2 \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} I_3 \qquad (1A)$$

$$I_3 + I \xrightarrow{k'_2} I_2 + I_2 \qquad (2A)$$

The formation of the comlex, I_3, is an equilibrium process with an equilibrium constant, K equal to

$$\frac{[I_3]}{[I][I_2]} = K = e^{\Delta S^0_1{}^0/R} \; e^{-\Delta H^0_1{}^0/RT} \qquad (3A)$$

where $\Delta S^0_1{}^0$ and $\Delta H^0_1{}^0$ represent the molar entropy and enthalpy, respectively, for the equlibrium process and where the brackets, [ ], represent the molar concentration of the species enclosed. Because the rate-controlling step is the atom transfer reaction of rate k_2, the overall rate is given by

$$\frac{-d\,I}{dt} = Kk'_2[I]^2[I_2] \qquad (4A)$$

The observed rate of reaction, k_3, is thus a composite of two constants:

$$k_3 = Kk_2 = A_2 \, e^{\Delta S^0_1{}^0/R} \; e^{-(E_2 + \Delta H^0_1{}^0)/RT} \qquad (5A)$$

where A_2 and E_2 represent, respectively, the Arrhenius A-factor and activation energy for the atom transfer reaction. If this reaction is

considered to be typical of its kind, E_2 is nearly zero and A_2 has a value of $10^{10.5}$ $M^{-1}sec^{-1}$ (Benson and Demore, 1965). If these values are inserted, Eq. 5A can be rearranged to give

$$\text{Log}_{10}\ k_3 = 10.5 + \frac{\Delta S^0{}_1{}^0}{4.56} - \frac{\Delta H^0{}_1{}^0}{4.56T} \qquad (6A)$$

The value of entropy, $\Delta S^0{}_1{}^0$ (in pressure units) is expected to be on the order of -30 Gibbs/mole, indicative of a tight complex (Benson, 1968). This estimate is supported by a comparison with entropy changes in analogous reactions, e.g., $O + O_2 \rightarrow O_3$, $\Delta S_0 \sim -30$ Gibbs/mole. The conversion of this entropy change to molar units gives $\Delta S^0{}_1{}^0 \sim -22$ Gibbs/mole. From these these values, the activation energy ($\Delta H^0{}_1{}^0$) for the flash photolysis study at 293°K can be estimated using Eq. 6A and the average of the best values for k_3 (values d and e, Table II) to be:

$$\text{Log}_{10}\ 2.5 \times 10^{12} = 10.5 + \frac{(-22)}{4.56} - \frac{\Delta H^0{}_1{}^0}{4.56(293)} \qquad (7A)$$

Thus, the low-temperature flash photolysis experiments are consistent with an activation energy of ~-9.0 kcal/mole, in agreement with the activation energy suggested by the results of the present study.

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FIGURE CAPTIONS

Figure 1. Schematic diagram of optical system for stochastic photolysis measurement of iodine atom recombination. Top: side view of laser source showing separation of photolysis (488 nm) and probe (514.5 nm) beams. Bottom: top view of apparatus for modulating photolysis beam and for recombining beams.

Figure 2. Iodine vapor cell used in stochastic photolysis experiments.

Figure 3. Fluorescence spectra of I_2 excited by 514.5 nm laser radiation. Peak at 514.5 nm in both spectra is caused by scattering of 514.5 nm laser line. Laser operated in all-lines mode at 4 W output power. A Top spectrum: I_2 pressure = 5 Torr; Ar pressure = 100 Torr. Curve 1, 488 nm laser radiation on; curve 2, 488 nm laser radiation off. B Bottom spectrum: I_2 pressure = 35 Torr; no Ar present.

Figure 4. Block diagram of electronic system for stochastic photolysis of I_2 vapor.

Figure 5. High-voltage amplifier used to drive Pockels cell for modulating photolysis beam.

Figure 6. Photometric amplifier useful in stochastic photolysis.

Figure 7. Typical kinetic decay curve for recombination of photolytically generated iodine atoms. Obtained from cross correlator during stochastic photolysis.

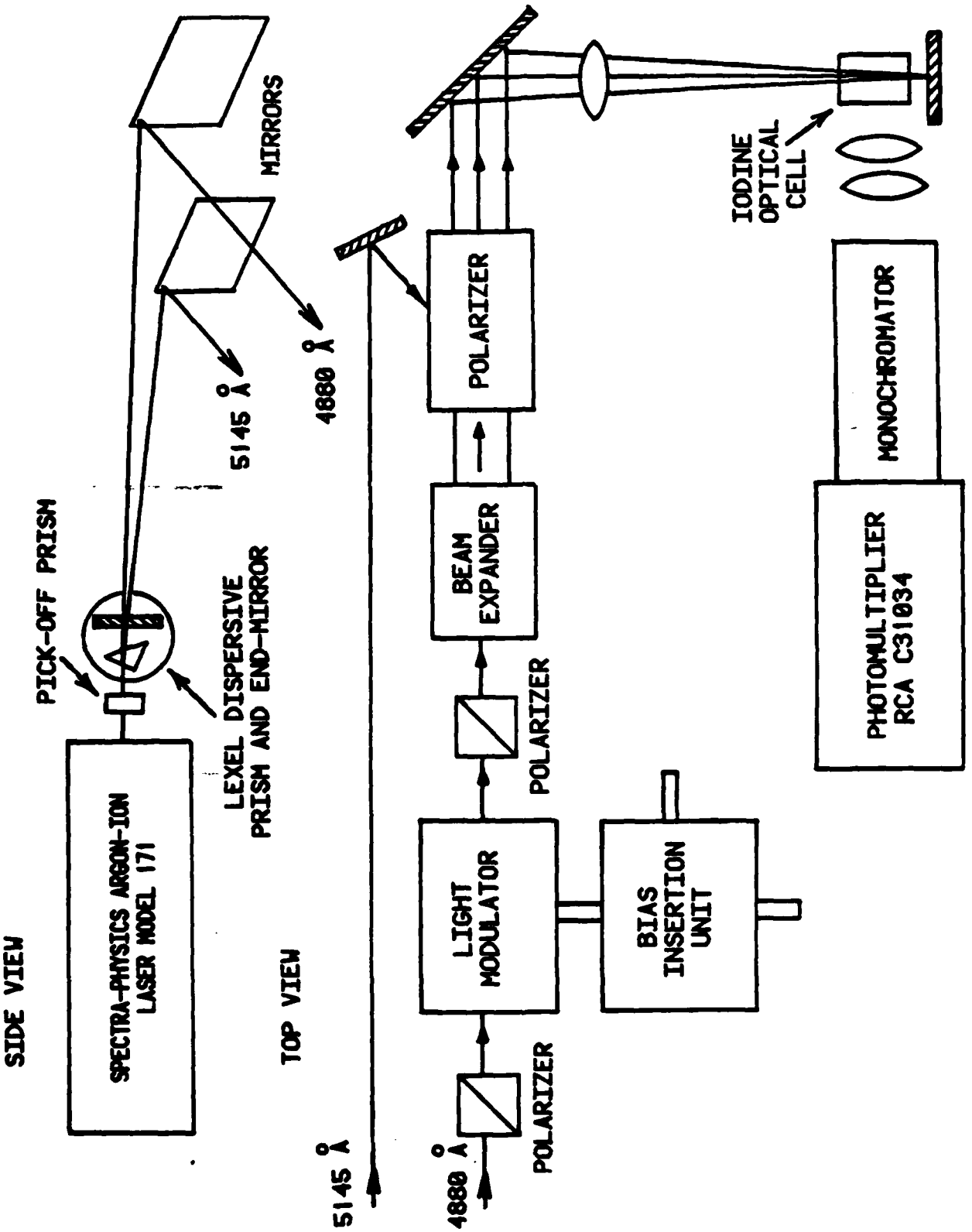
SIDE VIEW
SPECTRA-PHYSICS ARGON-ION LASER MODEL 171
PICK-OFF PRISM
LEXEL DISPERSIVE PRISM AND END-MIRROR
MIRRORS
5145 Å
4880 Å
TOP VIEW
5145 Å
4880 Å
POLARIZER
LIGHT MODULATOR
BIAS INSERTION UNIT
POLARIZER
BEAM EXPANDER
POLARIZER
IODINE OPTICAL CELL
MONOCHROMATOR
PHOTOMULTIPLIER RCA C31034

Figure 1

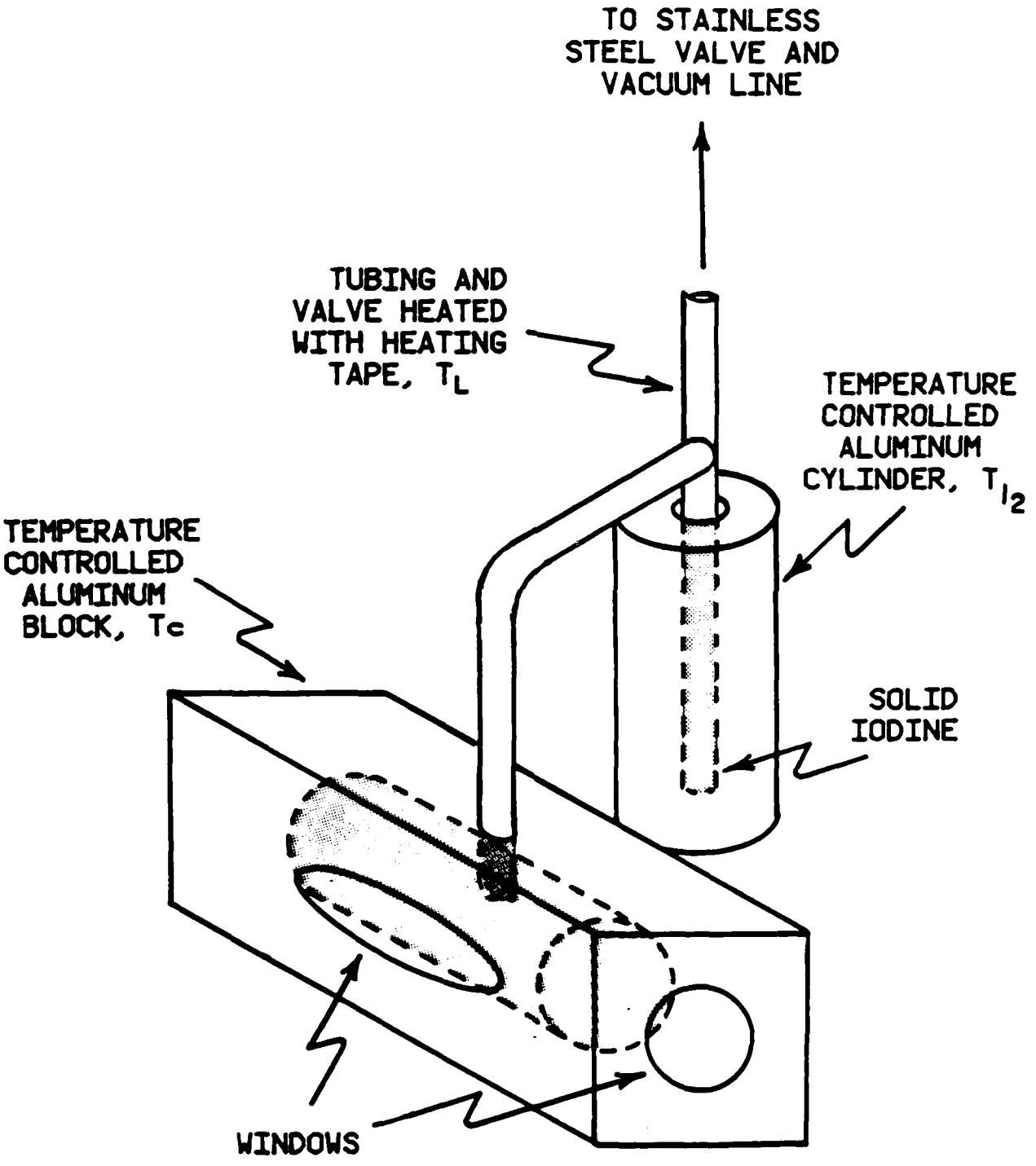
TO STAINLESS STEEL VALVE AND VACUUM LINE
TUBING AND VALVE HEATED WITH HEATING TAPE, T_L
TEMPERATURE CONTROLLED ALUMINUM CYLINDER, T_{I_2}
TEMPERATURE CONTROLLED ALUMINUM BLOCK, Tc
SOLID IODINE
WINDOWS

Figure 2

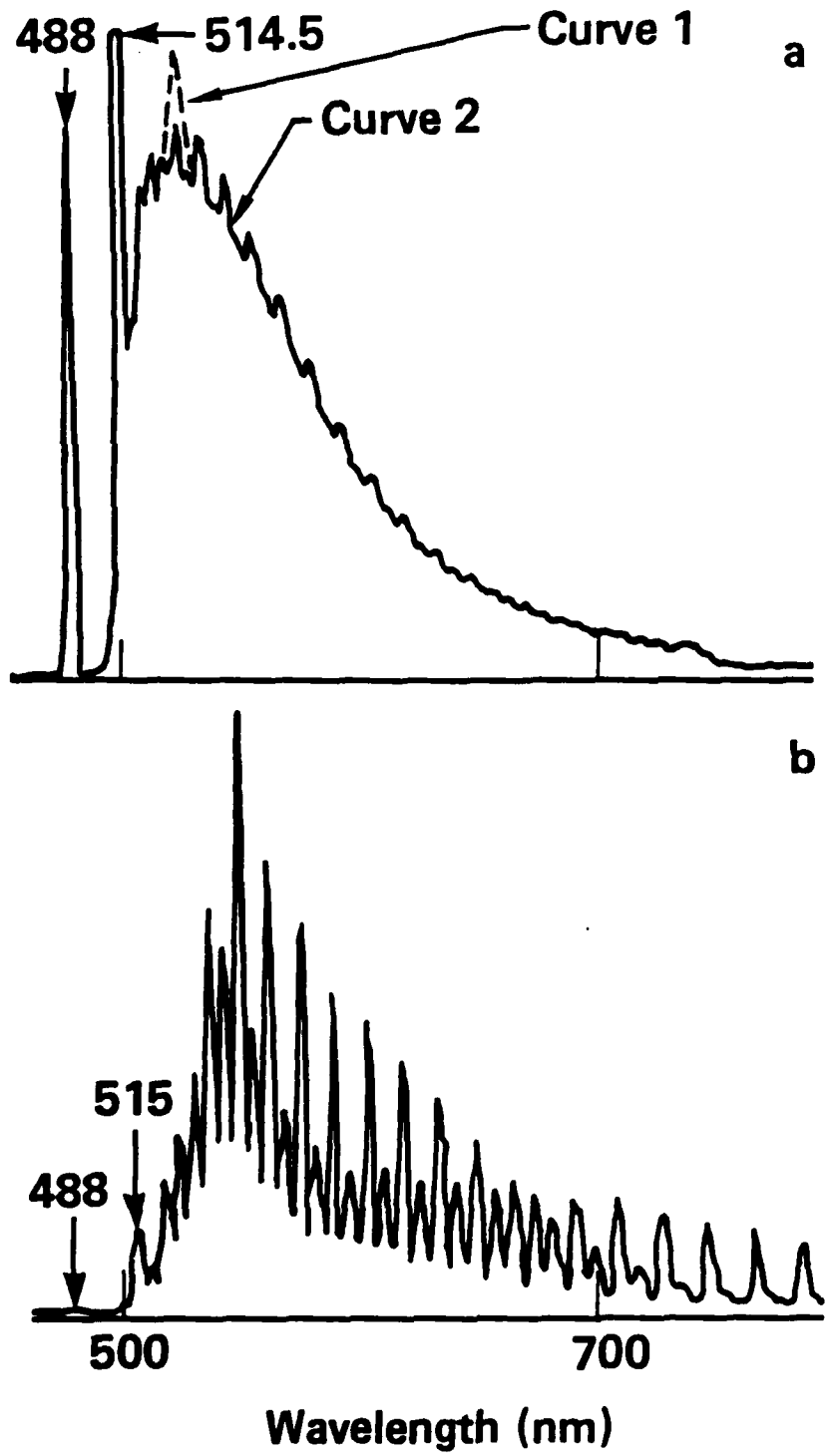

Figure 3

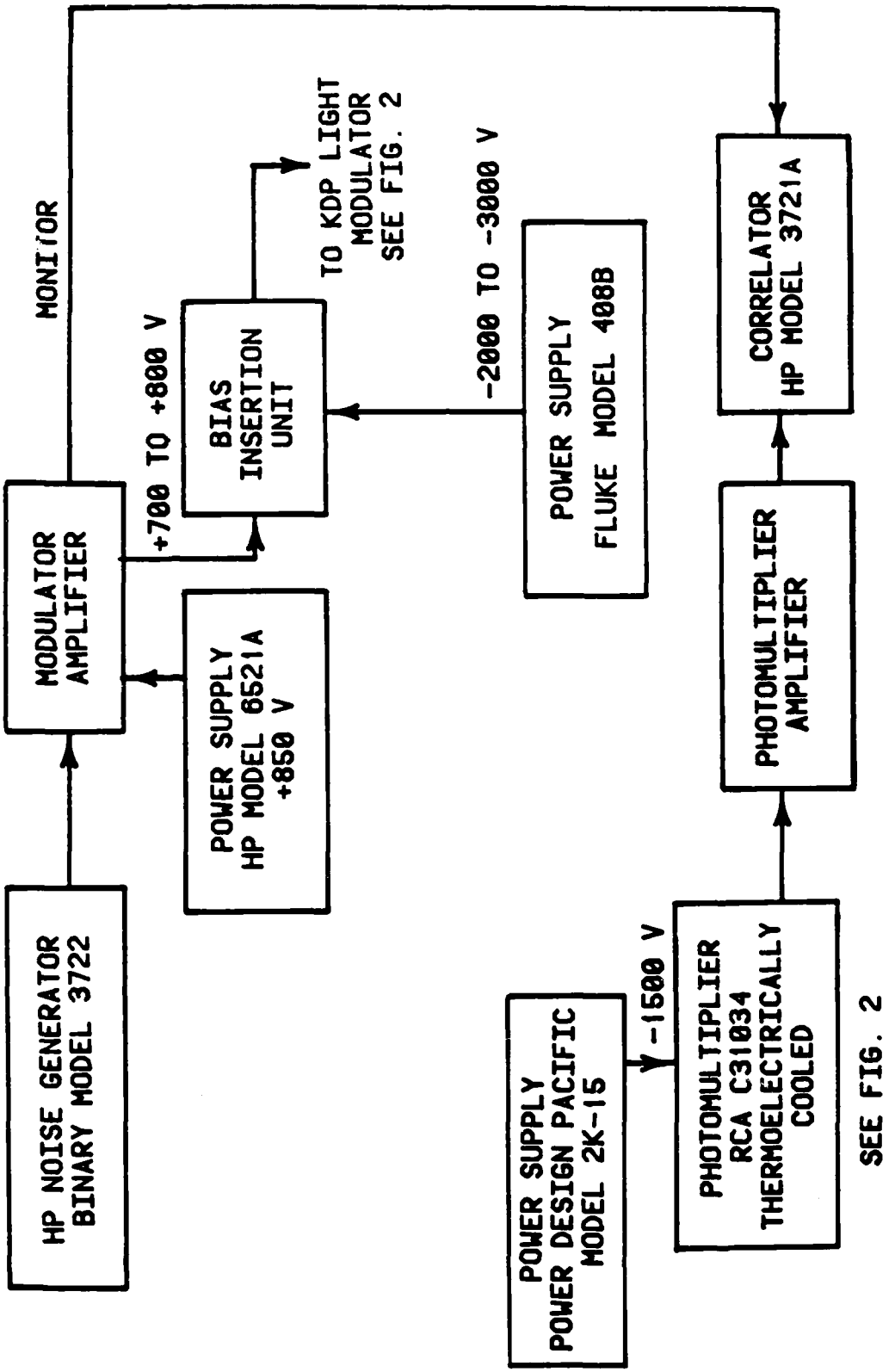
HP NOISE GENERATOR
BINARY MODEL 3722
MODULATOR
AMPLIFIER
POWER SUPPLY
HP MODEL 6521A
+850 V
+700 TO +800 V
BIAS
INSERTION
UNIT
TO KDP LIGHT
MODULATOR
SEE FIG. 2
MONITOR
-2000 TO -3000 V
POWER SUPPLY
FLUKE MODEL 408B
CORRELATOR
HP MODEL 3721A
PHOTOMULTIPLIER
AMPLIFIER
-1500 V
POWER SUPPLY
POWER DESIGN PACIFIC
MODEL 2K-15
PHOTOMULTIPLIER
RCA C31034
THERMOELECTRICALLY
COOLED
SEE FIG. 2

Figure 4

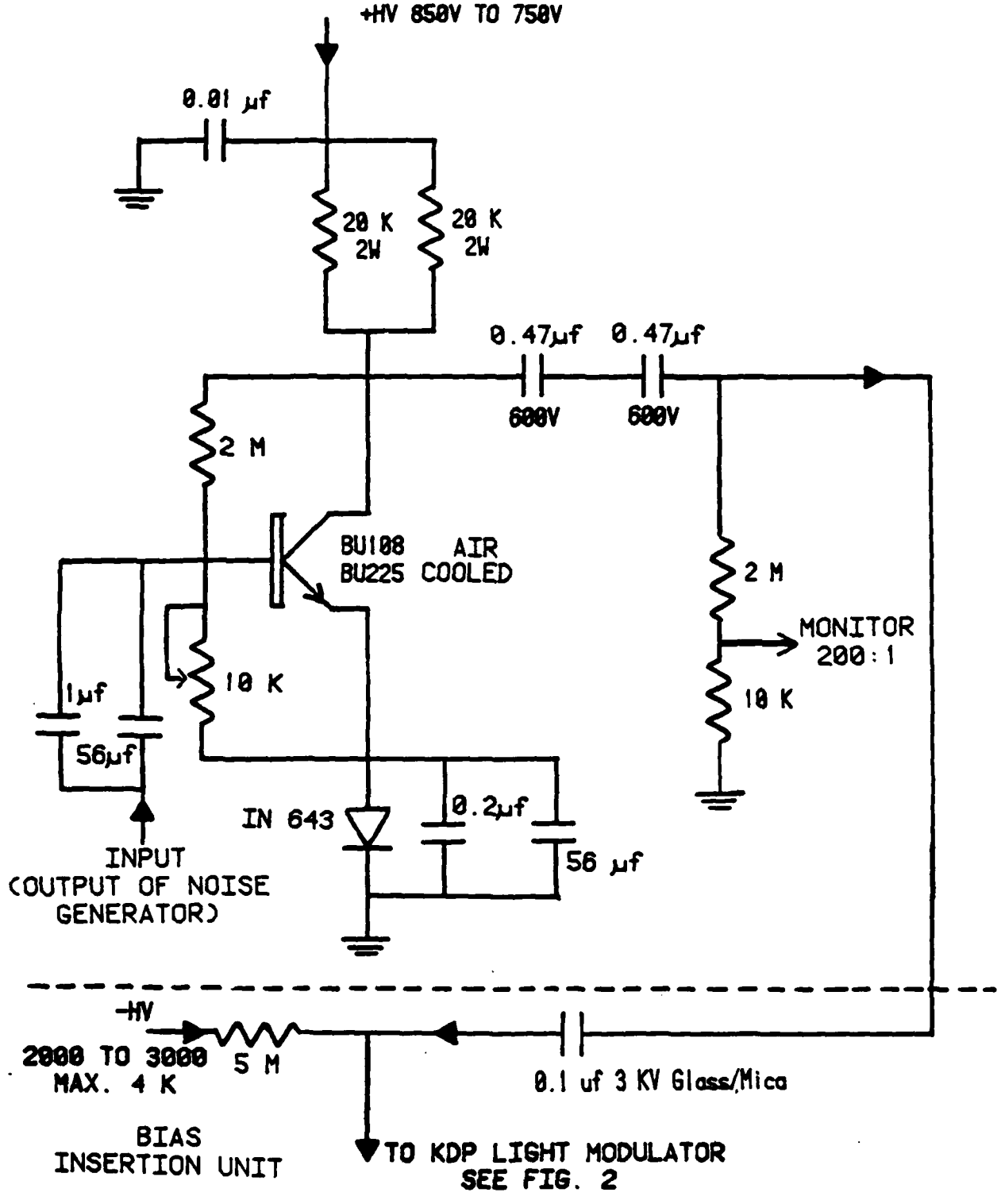
+HV 850V TO 750V
0.01 µf
20 K 2W
20 K 2W
0.47µf
0.47µf
600V
600V
2 M
BU108 AIR
BU225 COOLED
2 M
MONITOR 200:1
10 K
10 K
1µf
56µf
IN 643
0.2µf
56 µf
INPUT (OUTPUT OF NOISE GENERATOR)
-HV
2000 TO 3000
MAX. 4 K
5 M
0.1 uf 3 KV Glass/Mica
BIAS INSERTION UNIT
TO KDP LIGHT MODULATOR SEE FIG. 2

Figure 5

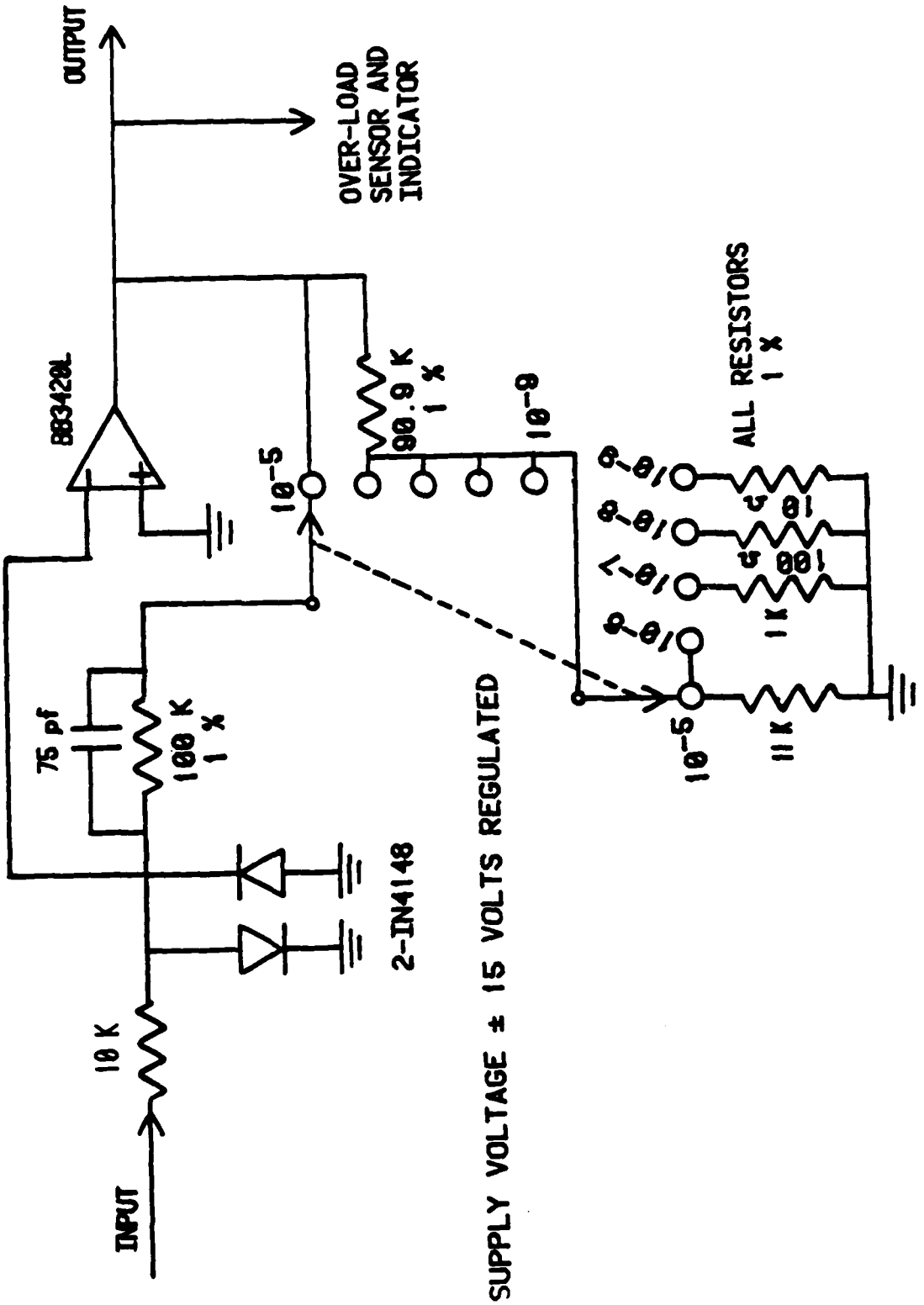
OUTPUT
OVER-LOAD SENSOR AND INDICATOR
883420L
10^{-5}
90.9 K 1 %
10^{-9}
ALL RESISTORS 1 %
11 K
75 pf
100 K 1 %
2-IN4148
10 K
INPUT
SUPPLY VOLTAGE ± 15 VOLTS REGULATED

Figure 6

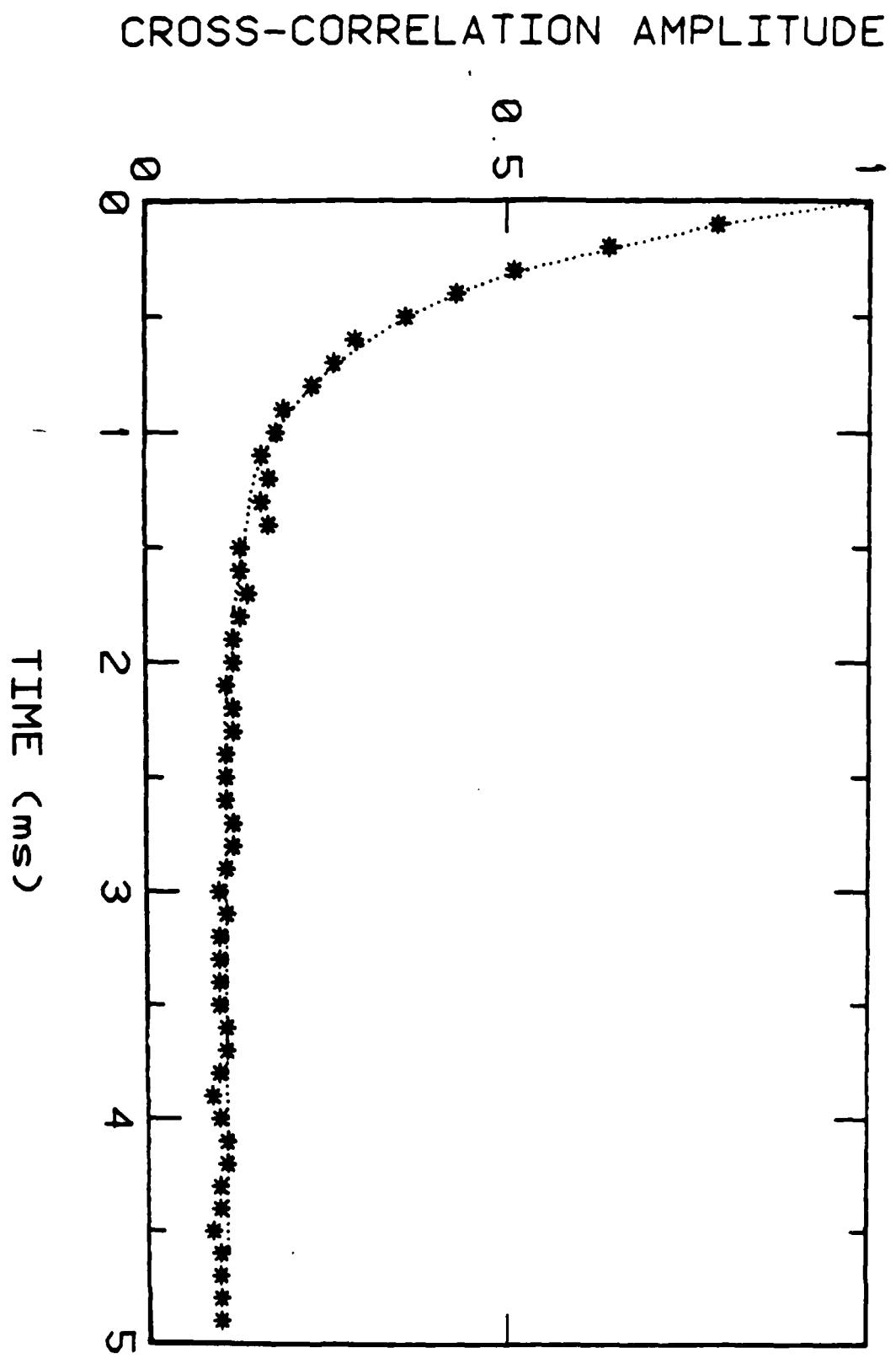

Figure 7

Table I. Calculated rate constant for recombination of iodine atoms with iodine molecules as third body.

I_2 Press. Torr	Cell Temp. ^oK	Half-life ($t_{\frac{1}{2}}$) of Correlation function ms	[Ar] mM	R	Argon rate constant, k_2 M^{-2} sec^{-1}	Calc. rate constant, k_3 M^{-2} sec^{-1}
0.81[b]	338	0.725	4.74	0.20	4.33×10^9 [a]	3.1×10^{11}
0.55[b]	305	0.395	5.26	0.20	5.50×10^9 [a]	1.8×10^{12}

[a]Porter and Smith, 1961; average of all studies.

[b]Calculated from Eq. 8 and measured temperature of iodine crystals.

Table II. Comparison of iodine atom recombination rate constants.

Measurement Technique	Rate Constant, k_3, M^{-2} sec^{-1}					
	293°K		305°K		338°K	
Noise Source			1.8×10^{12}		3.1×10^{11}	
Pulse Source	1.300×10^{12}	(a)	1.6×10^{12}	(d)	7.9×10^{11}	(d)
	1.700×10^{12}	(b)	2.0×10^{12}	(e)	8.3×10^{11}	(e)
	0.850×10^{12}	(c)				
	$2.100 \pm .230 \times 10^{12}$	(d)				
	2.80×10^{12}	(e)				

[a]Strong, et al., 1957.

[b]Christie, et al., 1955.

[c]Marshall and Davidson, 1953.

[d]Bunker and Davidson, 1958.

[e]Porter and Smith,1961.

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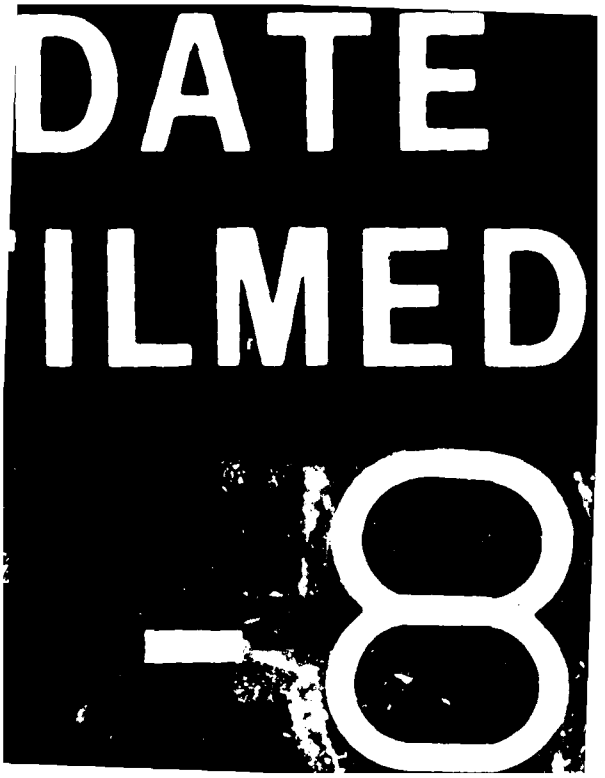
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